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(54) Title: POLYOL COMBINATION

(57) Abstract: Polyol combination for producing visco-elastic foams comprising up to a total of 100 parts by weight (pbw): (a) 30-70 pbw of a rigid polyol; and (b) 30-70 pbw of a polymer polyol component comprising up to a total of 100 wt.% (b1); 10-100 wt.% of a polymer polyol containing from 10 to 50 wt.% based on total weight of this polymer polyol of solid styrene-acrylonitrile polymer particles dispersed in a base polyol; and (b2) 0-90 wt.% of a polymer polyol containing 10-50 wt.% based on total weight of this polymer polyol of solid polystyrene particles dispersed in a base polyol. The polyol combination may additionally comprise up to 50 pbw of a polyether polyol having a molecular weight in the range of from 2500 to 6500, a functionality in the range of from 2.5 to 6, a hydroxyl value in the range of from 30 to 100 and a primary hydroxyl content of at least 40%. A visco-elastic foam may be obtained by reacting the polyol combination with a polyisocyanate component in the presence of from 1 to 5 pbw of water and at least one catalyst. The usual auxiliaries may also be present.

POLYOL COMBINATION

The present invention concerns a polyol combination for the preparation of low density viscoelastic foams, a process for the preparation of such foam, the foam itself and shaped articles comprising the foam.

5 Viscoelastic polyurethane foam (also sometimes referred to as low resilience foam or energy absorbing foam) is a type of flexible polyurethane foam which is characterised by a slow recovery from deformation and a high vibration damping. Such properties permit a
10 widespread use for the foam type in medical, packaging, automotive and sporting goods products. Specific applications include bedding and furniture applications, especially mattresses for bed-bound hospital patients or cushions for wheel chair users, toys and sports wear
15 protection.

 Low density viscoelastic foams, i.e. foams having a density less than 50 kg/m^3 , retaining good hardness, hysteresis and energy absorption qualities, are commercially attractive, not only because of these
20 qualities, but also because less raw material is required than for higher density foams.

 In WO-A-98/16567 a polyol combination for the preparation of an energy absorbing foam is disclosed comprising, to a total of 100 parts by weight,
25 (a) from 30 to 70 parts by weight of a polyol having a molecular weight in the range of from 2500 to 6500, a functionality in the range of from 2.5 to 6 and a primary hydroxyl content of at least 40%, optionally with a polymer stably dispersed therein; in conjunction or
30 association with

(b) from 70 to 30 parts by weight of a rigid polyol having a molecular weight in the range of from 300 to 1000, a functionality in the range of from 2.5 to 6.0 and a hydroxyl value in the range of from 200 to 600.

5 Although the above polyol combination results in low density viscoelastic foams having very good properties in terms of hardness, hysteresis and energy absorption, there is still room for further improvement.

10 The present invention aims to provide a polyol combination which results in low density viscoelastic foams having at least the same quality of the foams disclosed in WO-A-98/16567. The present invention especially aims at slightly improving the load deflection properties of the viscoelastic foams obtained.

15 These objects have been achieved by a polyol combination comprising one or two specific polymer polyols in combination with a rigid polyol.

Accordingly, the present invention relates to a polyol combination for producing visco-elastic foams comprising up to a total of 100 parts by weight (pbw):
20 (a) 30-70 pbw of a rigid polyol having a hydroxyl value in the range of from 200 to 600 mg KOH/g, a nominal average functionality in the range of from 2.5 to 6 and a molecular weight in the range of from 300 to 1000; and
25 (b) 30-70 pbw of a polymer polyol component comprising up to a total of 100 wt%

(b1) 10-100 wt% of a polymer polyol containing from 10 to 50 wt% based on total weight of this polymer polyol of solid styrene-acrylonitrile polymer particles
30 dispersed in a base polyol having a molecular weight in the range of from 2500 to 7000, an ethylene oxide content of at most 25 wt% based on total weight of this base polyol and a primary hydroxyl content of 10% or less (hereinafter "said SAN polymer polyol"), and

(b2) 0-90 wt% of a polymer polyol containing 10-50 wt% based on total weight of this polymer polyol of solid polystyrene particles dispersed in a base polyol having a molecular weight of from 2500 to 7000, an OH value of from 20 to 100 mg KOH/g, an ethylene oxide content in the range of from 5 to 40 wt% based on total weight of this base polyol, a primary hydroxyl content of at least 50% and a functionality of at least 2.5 (hereinafter "said POS polymer polyol").

The above polyol combination suitably comprises, up to a total of 100 pbw, 50-70 pbw of component (a) and 30-50 pbw of component (b).

The rigid polyol component (a) has a relatively low functionality and molecular weight. The polyol is required to have a molecular weight in the range of from 300 to 1000, preferably 500 to 800, a functionality in the range of from 2.5 to 6, preferably from 2.5 to 4, and a hydroxyl value in the range of from 200 to 600, preferably 200 to 450. The rigid polyol is most suitably based on propylene oxide as the only alkylene oxide, although ethylene oxide may in addition be used in amounts up to 40% by weight based on total alkylene oxide used.

In general, a polymer polyol is a dispersion of a solid polymer in a liquid polyol. Such systems are well known in the art and are normally prepared by polymerising one or more ethylenically unsaturated monomers in the presence of a free radical catalyst. Examples of such polymer polyol systems and methods for their preparation are disclosed in, for example, European Patent Specifications Nos. 0,076,491; 0,343,907 and 0,495,551.

Said SAN polymer polyol used as component (b1), accordingly, is a dispersion of 10 to 50 wt%, preferably 25 to 45 wt%, based on total weight of said SAN polymer

polyol of styrene-acrylonitril copolymer particles in a base polyol having the properties as indicated above. A preferred base polyol has a molecular weight in the range of from 2500 to 4000, an ethylene oxide content in the range of from 5 to 20 wt%, whereby the ethylene oxide is randomly distributed, and a primary hydroxyl content of 5% or less. The OH value of the base polyol is not particularly critical and may range from 10 to 200 mg KOH/g, suitably from 20 to 150 mg KOH/g. Preferably said OH value does not exceed 100 mg KOH/g and more preferably does not exceed 55 mg KOH/g.

Said POS polymer polyol used as component (b2) contains from 10 to 50 wt%, preferably from 15 to 40 wt%, based on total weight of this polymer polyol of solid polystyrene particles dispersed in a base polyol having the properties as indicated above. The preferred base polyol of said POS polymer polyol has a molecular weight in the range of from 4000 to 6000, an ethylene oxide content in the range of from 10 to 20 wt%, whereby the ethylene oxide is incorporated by tipping and hence is present as terminal poly(oxyethylene) moieties, and a primary hydroxyl content in the range of from 70 to 95%. The OH value of the base polyol of said POS polymer polyol is not particularly critical and will suitably be in the same ranges as indicated above for the base polyol of the SAN polymer polyol.

In one embodiment of the present invention the polymer component (b) exclusively comprises said SAN polymer polyol. In another, more preferred embodiment, however, the polymer component (b) comprises 20-80 wt% of said SAN polymer polyol and 20-80 wt% of said POS polymer polyol. In this embodiment it is preferred that said SAN polymer polyol is present in an amount of from 45 to 80 wt% with said POS polymer polyol being present in the remaining amount up to 100 wt%.

In a further preferred embodiment of the present invention the present polyol combination comprises in addition to components (a) and (b) ("php" refers to the amount in parts by weight per 100 parts by weight of polyol components (a) plus (b)):

(c) up to 50 php of a polyether polyol having a molecular weight in the range of from 2500 to 6500, a functionality in the range of from 2.5 to 6, a hydroxyl value in the range of from 30 to 100 and a primary hydroxyl content of at least 40%.

If this component (c) is present it is preferred that component (b) exclusively comprises said SAN polymer polyol. However, a polyol combination comprising the rigid polyol, said SAN polymer polyol, said POS polymer polyol and the above defined component (c) is also feasible and will also result in a viscoelastic foam having excellent load deflection properties.

Preferred polyol components (c) are those having in addition an ethylene oxide content in the range of from 5 to 50% by weight, preferably from 10 to 30% by weight and more preferably 15 to 25% by weight. It has been found particularly advantageous to use polyols having a molecular weight in the range of from 4,000 to 6,000, and a primary hydroxyl content in the range of from 50 to 100%, more preferably from 70 to 95%. The OH value of the polyol component (c) may range from 10 to 200 mg KOH/g, suitably from 20 to 150 mg KOH/g. Preferably said OH value does not exceed 100 mg KOH/g and more preferably does not exceed 55 mg KOH/g.

The polyol components (a), (b) and (c) may be used one in conjunction with the other or combined as a polyol blend in the preparation of viscoelastic foam. If used in a blend other components may be included as well, thus resulting in a polyol formulation. Such formulation typically comprises in addition to the polyol combination

a blowing agent (preferably water), a polyurethane catalyst and optionally a cross-linking agent.

Auxiliaries like fillers, flame retardants, foam stabilisers, and colourants may be present as well.

5 Conveniently, the polyol formulation further comprises:

(d) 1 to 5 php of water;

(e) 0.01 to 2 php of a polyurethane catalyst; and

(f) 0 to 3.0 php of a cross-linking agent.

10 In a second aspect the present invention relates to a process for the preparation of a visco-elastic foam, which process comprises reacting

(a) the polyol combination as defined herein before,

(b) a polyisocyanate component, which is used in such amount that the isocyanate index is in the range of from

15 70 to 120, preferably 70 to 100, and

(c) from 1 to 5 php of water,

in the presence of at least one catalyst and optionally usual auxiliaries.

Polyisocyanates that may be used are those
20 conventionally applied in the production of flexible polyurethane foams. Useful polyisocyanates should contain at least two isocyanate groups and include both aliphatic -usually alkylene- and aromatic di-, tri-, tetra- and higher isocyanates known in the art to be suitably
25 applied in the production of flexible polyurethane foams. Mixtures of two or more of such aliphatic and/or aromatic polyisocyanates may also be applied. Examples of suitably polyisocyanates, then, include 2,4-toluene diisocyanate (2,4-TDI), 2,6-TDI, mixtures of 2,4-TDI and 2,6-TDI,
30 1,5-naphthene diisocyanate, 2,4-methoxyphenyl diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), 4,4'-biphenylene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate and 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate,
35 diisocyanate, 4,4',4''-triphenylmethane triisocyanate,

2,4,6-toluene triisocyanate, 4,4'-dimethyl-2,2',5,5'-diphenylmethane tetraisocyanate, polymethylene-polyphenylene polyisocyanate and mixtures of two or more of these. Polymeric MDI, a mixture of polyisocyanates with
5 MDI as the main component, may also be used. For the purpose of the present invention it has been found particularly advantageous to use TDI as the polyisocyanate component. More specifically, the use of 2,4-TDI, 2,6-TDI or a mixture thereof is preferred. Very good
10 results have been attained with a mixture of 2,4-TDI and 2,6-TDI in a weight ratio 2,4-TDI:2,6-TDI of about 80:20 or 65:35.

Water is used in an amount of from 1 to 5 php and serves as a (chemical) blowing agent. Water reacts with
15 isocyanate groups according to the well known NCO/H₂O reaction, thereby releasing carbon dioxide which causes the blowing to occur. In addition to water a conventional blowing agent may be used. Such conventional blowing agents include (liquid) carbon dioxide, halogenated
20 hydrocarbons (HCFC's and HFC's), aliphatic alkanes (e.g. pentane, isopentane) and alicyclic alkanes (e.g. cyclopentane). If used at all, the additional blowing agent will be typically be used in an amount of from about 0.1 to 15 php in case of halogenated hydrocarbons,
25 aliphatic alkanes, alicyclic alkanes and liquid carbon dioxide.

Polyurethane catalysts are known in the art and include many different compounds. An extensive list of polyurethane catalysts is, for instance, given in U.S.
30 Patent Specification No. 5,011,908. For the purpose of the present invention, however, it has been found particularly advantageous to use both an amine catalyst and a tin catalyst. Tin catalysts include tin salts and dialkyl tin salts of carboxylic acids, such as stannous

octoate, stannous oleate, dibutyltin dilaureate, dibutyltin acetate and dibutyltin diacetate. Of these stannous octoate and dibutyltin dilaureate are most frequently applied. The tin catalyst most preferably applied for the purpose of the present invention is stannous octoate, as this catalyst has been found to result in a flexible foam having excellent properties, particularly in terms of resilience and density. In stead of or in addition to the tin catalyst, one or more tertiary amine catalysts may also be applied. Such tertiary amine catalysts are widely used and include, for instance, bis(2,2'-dimethyl-amino)ethyl ether, trimethylamine, triethylamine, triethylenediamine and dimethylethanolamine. Examples of commercially available tertiary amine catalysts are those sold under the trade names NIAX, TEGOAMIN and DABCO (all trade marks). The catalyst is typically used in an amount of from 0.01 to 2.0 php. Preferred total amounts of catalyst are from 0.05 to 1.0 php.

The use of cross-linking agents in the production of polyurethane foams is well known. Polyfunctional glycol amines are known to be useful for this purpose. The polyfunctional glycol amine which is most frequently used is diethanolamine, often abbreviated as DEOA. If used at all, the cross-linking agent is applied in amounts up to 3.0 php, for example from 0.2 to 1.5 php. However, it is a special feature of the present invention that no separate cross linking agent need be used to ensure good foam formation.

In addition, other well known auxiliaries, such as flame retardants, foam stabilisers (surfactants) and fillers may also be used. Organosilicone surfactants are most conventionally applied as foam stabilisers in polyurethane production. A large variety of such organosilicone surfactants is commercially available.

Usually, such foam stabiliser is used in an amount of up to 5% by weight based on the reaction mixture of polyol combination and polyisocyanate component.

5 The process of the second aspect can be carried out
in the conventional ways and under the normal conditions
known in the art. This can include both slabstock and
moulding techniques. Typically this includes mixing all
components but the polyisocyanate together, then adding
the polyisocyanate component while mixing and finally
10 pouring the resulting foaming mixture on a moving belt or
in a box to prepare the viscoelastic foam. The resulting
blocks can subsequently be cut into the desired shape.
Mixing the components and pouring the foaming mixture
into the mould is typically carried out at ambient
15 temperature and pressure.

In a third aspect the present invention relates to
viscoelastic foams obtainable by the process of the
second aspect of the present invention as described
herein before.

20 The viscoelastic foam of the present invention is
especially useful for application in mattresses and
cushioning (particularly for use with the bedridden or
hospitalised), packaging and orthopaedic appliances.
Other uses of the foam of the invention include
25 protective clothing for motorcyclists, helmets, and sound
absorbing items such as ear plugs.

In mattresses, cushioning and related items, the
viscoelastic foam provides a useful material, as it
becomes softer under the action of body heat so that it
30 takes the shape of the body and provides improved comfort
by distribution of the compression load over the foam.
The open celled nature of the foam provides necessary
ventilation, and the high hysteresis means that after
use, the foam article will gradually (slowly) revert to
35 its original shape.

The present invention therefore in a final aspect also relates to shaped articles comprising the energy absorbing foam of the invention. Such shaped articles, for example, include cushions for wheel chairs, and
5 mattresses formed of a composite foam having, as a surface layer, the energy absorbing foam of the invention.

The invention is further illustrated by the following examples. In these examples the following components are
10 used.

Polyol I: a rigid PO-based polyether polyol having an OH value of 250 mg KOH/g, a molecular weight of 675, and a nominal average functionality of 3.

Polyol II: a polyol being a EO/PO based polyether
15 polyol having a primary hydroxyl content of 80%, an EO-content (tipped) of 14 wt% based on total weight of base polyol, a nominal average functionality of 3, a molecular weight of 4700 and an OH value of 36 mg KOH/g

PP-A: a polymer polyol containing (i) a base polyol
20 being a EO/PO based polyether polyol having a primary hydroxyl content of essentially 0%, an EO-content (random) of 14 wt% based on total weight of base polyol, a nominal average functionality of 3, a molecular weight of 3500 and an OH value of 33 mg KOH/g and and (ii)
25 stably dispersed therein 40 wt% styrene-acrylonitrile copolymer.

PP-B: a polymer polyol containing (i) a base polyol
being a EO/PO based polyether polyol having a primary
hydroxyl content of 80%, an EO-content (tipped) of 14 wt%
30 based on total weight of base polyol, a nominal average functionality of 3, a molecular weight of 4700 and an OH value of 30 mg KOH/g and (ii) stably dispersed therein
15 wt% polystyrene particles.

T80: refers to DESMODUR T80, a 80/20 weight % mixture of 2,4 and 2,6 toluene diisocyanate (DESMODUR is a trademark).

5 B8002: refers to TEGOSTAB B8002, a silicone surfactant ex Goldschmidt (TEGOSTAB is a trademark).

NIAX A-1: 70% bis-dimethylaminoethylether in dipropylene glycol (amine catalyst; NIAX is a trademark).

DABCO 33LV: 33% triethylene diamine in dipropylene glycol (amine catalyst; DABCO is a trademark).

10 The tests performed were carried out on foam samples of 20x30x15 cm. The tests applied were determination of the compression load deflection (CLD), also sometimes referred to as hardness (as e.g. in WO-A-98/16567), in accordance with DIN 53577 and the indentation load
15 deflection (ILD) at 25%, 40% and 65% compression according to DIN 53576B. For both CLD and ILD test the speed for testing was 20 mm/min. The density was determined in accordance with ASTM 3574-77.

Example 1 and Comparative Example C-1

20 Foams were prepared in a conventional manner by first blending the ancillary chemicals (i.e. DABCO 33LV, NIAX A-1, B8002) with the polyols in a manifold followed by mixing with the polyisocyanate. The polyol formulation and the polyisocyanate were kept at a temperature between
25 20 and 23 °C. After the foams had been formed, they were left to cure for one week before cutting foam samples (20x30x15 cm). Subsequently the foam samples were conditioned for 16 hours at 23 °C and 50% relative humidity before testing.

30 The foam of Example 1 was prepared using a polyol combination consisting of 60 pbw of rigid polyol, 20 pbw of PP-A (SAN polymer polyol) and 20 pbw of PP-B (POS polymer polyol). In Comparative Example 1 a polyol combination in accordance with WO-A-98/16567 was used

consisting of 60 pbw of rigid polyol and 40 pbw of POS polymer polyol.

The foam mixtures used and the foam properties are indicated in table 1.

5 Examples 2-4

Example 1 was repeated except that different amounts of the various polyol components were used. The foam mixtures used and the foam properties are indicated in table 1.

10 From Table 1 it can be seen that the foams according to the invention show an excellent combination of density, load deflection properties and resilience. The foam prepared in the Comparative Example 1 also has a good set of properties, but in comparison with the foam
15 of Example 1 exhibits a slightly higher resilience and a flatter ILD pattern with a higher ILD 25% and a lower ILD 65%. This means that the foam of Example 1 has a slightly softer initial touch (it takes less force to accomplish an initial compression), but at high compression gives
20 more resistance (i.e. a slightly higher force is needed to achieve 65% compression). This behaviour is also sometimes expressed by means of the support factor S:

$$S = \text{ILD } 65\% / \text{ILD } 25\%$$

It can be derived from Table 1 that the viscoelastic foam
25 of Example 1 has a slightly higher support factor (S= 2.3) than the foam of Comparative Example 1 (S= 2.0).

Table 1 Foam formulations and foam properties

Component	Example No.				
	1	C-1	2	3	4
Polyol I (pbw)	60	60	50	50	50
Polyol II (pbw)					25
PP-A (pbw)	20		25	40	25
PP-B (pbw)	20	40	25	10	
Water (pbw)	2	2	2	2	2
B8002 (pbw)	1.8	1.8	1.8	1.6	1.0
NIAX A-1 (pbw)	0.33	0.15	0.17	0.17	0.17
DABCO 33LV (pbw)	0.66	0.30	0.33	0.33	0.33
T80 (pbw)	35.91	35.81	33.20	33.26	33.39
Iso index	80	80	80	80	80
Foam Properties					
Density (kg/m ³)	44.75	45.03	44.65	44.18	44.48
CLD (kPa)	1.95	1.88	2.45	2.52	2.44
ILD 25% (N)	57	62	76	72	74
ILD 40% (N)	72	75	92	88	91
ILD 65% (N)	131	127	154	151	155
Resilience (%)	6	8	9	9	11

C L A I M S

1. Polyol combination for producing visco-elastic foams comprising up to a total of 100 parts by weight (pbw):

(a) 30-70 pbw of a rigid polyol having a hydroxyl value in the range of from 200 to 600 mg KOH/g, a nominal
5 average functionality in the range of from 2.5 to 6 and a molecular weight in the range of from 300 to 1000; and
(b) 30-70 pbw of a polymer polyol component comprising up to a total of 100 wt%

(b1) 10-100 wt% of a polymer polyol containing from
10 10 to 50 wt% based on total weight of this polymer polyol of solid styrene-acrylonitrile polymer particles dispersed in a base polyol having a molecular weight in the range of from 2500 to 7000, an ethylene oxide content of at most 25 wt% based on total weight of this base
15 polyol and a primary hydroxyl content of 10% or less (hereinafter "said SAN polymer polyol"), and

(b2) 0-90 wt% of a polymer polyol containing 10-50 wt% based on total weight of this polymer polyol of solid polystyrene particles dispersed in a base polyol
20 having a molecular weight of from 2500 to 7000, an OH value of from 20 to 100 mg KOH/g, an ethylene oxide content in the range of from 5 to 40 wt% based on total weight of this base polyol, a primary hydroxyl content of at least 50% and a functionality of at least 2.5
25 (hereinafter "said POS polymer polyol").

2. Polyol combination as claimed in claim 1 comprising, up to a total of 100 pbw, 50-70 pbw of component (a) and 30-50 pbw of component (b).

3. Polyol combination as claimed in claim 1 or 2,
30 wherein the rigid polyol has a molecular weight in the

range of from 500 to 800 and a hydroxyl value in the range of from 200 to 450.

4. Polyol combination as claimed in any one of the preceding claims, wherein said SAN polymer polyol
5 contains from 25 to 45 wt% based on total weight said SAN polymer polyol of solid styrene-acrylonitrile polymer particles.

5. Polyol combination as claimed in any one of the preceding claims, wherein the base polyol of said SAN
10 polymer polyol has a molecular weight in the range of from 2500 to 4000, an ethylene oxide content in the range of from 5 to 20 wt%, whereby the ethylene oxide is randomly distributed, and a primary hydroxyl content of 5% or less.

15 6. Polyol combination as claimed in any one of the preceding claims, wherein the base polyol of said POS polymer polyol has a molecular weight in the range of from 4000 to 6000, an ethylene oxide content in the range of from 10 to 20 wt%, whereby the ethylene oxide is
20 incorporated by tipping, and a primary hydroxyl content in the range of from 70 to 95%.

7. Polyol combination as claimed in any one of the preceding claims, wherein the polymer component (b) exclusively comprises said SAN polymer polyol.

25 8. Polyol combination as claimed in any one of claims 1-6, wherein the polymer component (b) comprises 20-80 wt% of said SAN polymer polyol and 20-80 wt% of said POS polymer polyol.

9. Polyol combination as claimed in any one of the preceding claims, wherein the combination additionally
30 comprises ("php" refers to the amount in parts by weight per 100 parts by weight of polyol components (a) plus (b))

(c) up to 50 php of a polyether polyol having a molecular
35 weight in the range of from 2500 to 6500, a functionality

in the range of from 2.5 to 6, a hydroxyl value in the range of from 30 to 100 and a primary hydroxyl content of at least 40%.

- 5 10. A process for the preparation of a visco-elastic foam, which process comprises reacting
- (a) the polyol combination as defined in any one of claims 1 to 9
- (b) a polyisocyanate component, which is used in such amount that the isocyanate index is in the range of from
- 10 70 to 120, and
- (c) from 1 to 5 php of water,
- in the presence of at least one catalyst and optionally usual auxiliaries.
- 15 11. Process as claimed in claim 10, wherein the polyisocyanate is toluene diisocyanate.
12. A visco-elastic foam obtainable by the process of claim 10 or 11.
13. A shaped article comprising the visco-elastic foam of claim 12.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 866 102 A (PRAY EDWARD R ET AL) 12 September 1989 (1989-09-12) column 1, line 24 -column 2, line 13 column 9 -column 11; example 1; table I	1-3,7, 10,12,13
A	US 5 248 704 A (ROSSIO RICHARD C ET AL) 28 September 1993 (1993-09-28) column 1, line 56 - line 68 column 8; example 1	1-3,7, 10,12,13
A	WO 98 16567 A (SHELL INT RESEARCH) 23 April 1998 (1998-04-23) cited in the application page 1, line 1 -page 4, line 1 page 9, line 1 - line 19 example 1; table 1	1,3,8, 10-13

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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